

COATINGS. ENAMELS

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EFFECT OF ENAMEL LAYER THICKNESS ON DEFECTIVENESS OF ENAMEL COATINGS

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The dependence of the oxidation rate of steel under a film of enamel at the firing temperatures of the enamel is examined. The size of the critical gas bubble which breaks through the enamel film during annealing is calculated and determined experimentally.

Key words: one-coat primer-free enameling, bubble streak defect, average rate of oxidation of steel.

At present the most cost-effective method of enameling a steel sheet is one-coat primer-free enameling. In this method of enameling there is a high danger of a bubble streak defect arising at the location of the weld seams on the article. The reason for such a defect is that particles of clay and small fractions of enamel with chemically bound water, which on drying are not removed and are released from the weld seams during firing, breaking through the enamel melt, are sucked with the slip water into the gap between the articles being welded together. In the locations where the metal surface is bared, the metal undergoes intense oxidation by the atmosphere. The iron beneath the layer of fused enamel is oxidized in the air atmosphere by water vapor dissolved in the melt with hydrogen being released [1].

The defects which break the continuity of the enamel coating weaken the protection of the metal from corrosive media and degrade the performance of the article. They are caused mainly by two factors — the appearance of a gas phase during firing as a result of physic-chemical processes at the metal – enamel boundary and stresses, after the enamel article has cooled, whose effect is determined by the difference of the linear thermal expansion coefficient of the materials. If the stresses can be avoided by matching the CLTEs, then the formation of a gas phase during firing is unavoidable, since it is due to the reaction occurring between the metal, enamel, and furnace atmosphere. Bubbles, pores, and

pin pricks can form on an enamel coating as a result of gas release.

One of the most effective methods of studying the defectiveness of an enamel coating is to combine optical microscopy with high-voltage flaw-detection, which makes it possible to determine the sizes and types of defects.

The present work is concerned with studying enameling defects using a corona discharge and determining the optimal thickness of the enamel layer for which spontaneous closure of pores occurs during the firing process.

An MBS-200 stereoscopic microscope, making it possible to obtain an image of the surface with magnification to $\times 200$, was used to study the defects of the enamel coating visually.

The study showed that the surface defects of the enamel coating are usually bubbles, most of which do not break the continuity of the enamel layer. But, there are also through defects. The bubble diameters range from 20 to 200 μm .

After visual examination the samples were examined by means of a corona discharge. A sharp needle was used as a flaw-detection probe. The corona discharge was accompanied by glowing of the air at the needle near defects, which was recorded visually and by video recording. A corona discharge makes it possible to record reliably the presence and arrangement of through defects and to calculate their number.

The area of the defects is $16 \times 10^{-4} - 9 \times 10^{-4} \text{ cm}^2$ for enamel coating thickness 0.15 mm and $10 \times 10^{-4} - 5 \times 10^{-4} \text{ cm}^2$ for 0.57 mm. The tests showed that as the thickness of the enamel layer increases, the breakdown voltage increases in a regular manner (Fig. 1).

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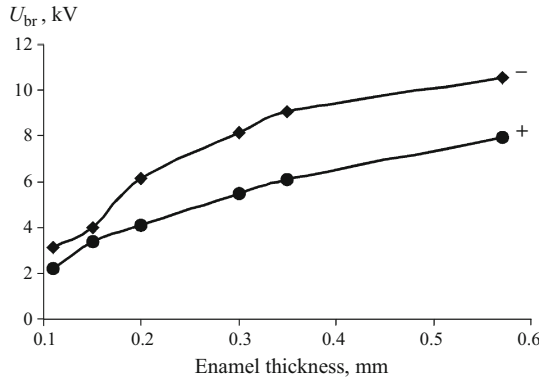


Fig. 1. Breakdown voltage versus the thickness of the enamel layer with positive and negative charges.

The dependence of the rate of oxidation of 08KP steel on the thickness of the glass melt with composition $0.33\text{Na}_2\text{O}$, 0.67SiO_2 was studied by continuous gravimetric weighing performed with a differential analyzer in an air-vapor atmosphere at vapor partial pressure 40 kPa and temperature 1273 K.

The corrosion rate of iron beneath the melt is limited by the diffusion permeability of the melt [3], which in the absence of natural convection in the film can be expressed by the equation

$$v = \Delta C D / \delta \approx \Delta C \gamma, \quad (1)$$

where D is the diffusion coefficient, cm^2/sec ; δ is the thickness of the film, cm; γ is the coefficient of mass transfer, K^{-1} ; and, ΔC is concentration gradient of the diffusing substance over the thickness of the film, mg/cm^3 .

We shall evaluate the possibility of natural convection appearing in the melt film on the basis of the fact [4] that in a thin film of incompressible fluid heated from below the condition for decay of the convective heat fluxes is given by Reynolds number

$$\text{Re} = g \beta \Delta T \delta^2 / (\lambda_c \nu) \leq 1708, \quad (2)$$

where g is the acceleration of gravity; β is the coefficient of volume expansion; ΔT is the temperature differential in the layer of liquid; δ is the thickness of the layer; λ_c is the thermal diffusivity; and, ν is the kinematic viscosity.

We shall evaluate the Reynolds number on the basis of the experimental data for $0.33\text{Na}_2\text{O} - 0.67\text{SiO}_2$ melt. According to [5] $\gamma = 10.3 \times 10^{-5} \text{K}^{-1}$ at 1273 K, and at the same temperature the viscosity $\eta = 128.8 \text{ dPa}$, the density $\rho = 2.22 \text{ g}/\text{cm}^3$, and $\nu = \eta/\rho = 5.8 \times 10^2 \text{ m}^2/\text{sec}$. The quantity $\lambda_c = \lambda/(C_p \rho)$, where λ is the thermal conductivity and C_p is the heat capacity. At 1273 K $C_p = 1.79 \text{ J}/(\text{g} \cdot \text{K})$ [5], $\lambda = 1.16 \text{ W}/(\text{m} \cdot \text{K})$ [5]. Hence $\lambda_c = 2.5 \times 10^{-7} \text{ m}^2/\text{sec}$. Let $\Delta T = 50 \text{ K}$, which is known to be greater than the actual value of ΔT . Then, for $\delta = 0.25 \text{ mm}$ we have $\text{Re} = 1.1$. There-

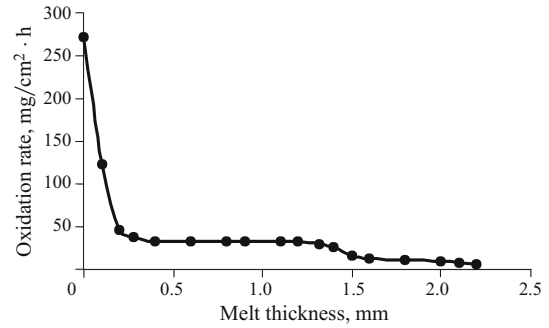
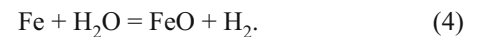


Fig. 2. Oxidation rate of steel versus the thickness of a layer of enamel melt.

fore, natural convection in the film cannot play a large role and can be neglected. If the convection developed by the released hydrogen bubbles is also neglected, then according to (1), as the film thickness increases, the rate of oxidation of iron should decrease evenly.

Let us now compare the result with experiment. A curve of $v - \delta$ is displayed in Fig. 2. It is evident that as the film thickness increases with $\delta \geq 0.2 \text{ mm}$ the oxidation rate decreases from 270 to $50 \text{ mg}/(\text{cm}^2 \cdot \text{h})$. Probably, for thickness $\delta < 0.2 \text{ mm}$ the film is rapidly enriched with iron oxides, which is what determines the high rate of oxidation via the reaction $\text{Fe} + 2\text{Fe}^{3+} = 3\text{Fe}^{2+}$. For δ from 0.4 to 1.2 mm the oxidation rate is practically independent of the film thickness, which can be explained as follows. When a hydrogen bubble breaks through the melt film, a crater forms in the film, and contact between the metal and the oxidative atmosphere is possible up to the moment when melt fills the bottom of the crater. In this time interval the iron comes into direct contact with oxidizers which leads to the reactions



After the crater bottom is filled with a thin layer of melt, oxidation of iron continues at a higher rate than at locations where it is covered by a melt film up to the entire thickness. Probably, for film thickness 0.4 – 1.2 mm the reactions (3) and (4) determine the total rate of oxidation. Indeed, for constant water vapor partial pressure the amount of vapor dissolved in the melt is constant. For this reason, the number of hydrogen bubbles released is approximately the same and therefore the oxidation rate should be the same. This result agrees with experiment. The decrease of the oxidation rate for $\delta > 1.2 \text{ mm}$ is probably due to the fact that for a larger thickness of the film some bubbles start to detach from the surface of the metal without denuding it. Moving in the volume of the film the bubbles give rise to mixing of the melt but at the same time they screen the metal. As follows from Fig. 2, above $\delta = 1.6 \text{ mm}$ the oxidation rate practically no longer depends on the thickness of the film.

The data obtained show that the critical size h of the bubbles which detach in the volume of the film is 1.2 – 1.6 mm. Taking approximately $2r_0 = \delta = h$, we find that the critical radius of the detached bubbles is $r_0 \approx 0.6 - 0.8$ mm.

We shall now evaluate r_0 using the well-known relation determining the conditions for adhesion of a bubble which is a part of a sphere with radius r_{cr} [6]:

$$2\pi r_{cr} \sigma_{liq} \sin \theta = V\rho + \pi r_0^2 (2\sigma_{liq}/\rho_0 - hgp), \quad (5)$$

where r_{cr} is the radius of the area of the base of a bubble; σ_{liq} and ρ are the surface tension and density of the melt; σ is the wetting angle for the melt; and, V and h are the volume and height of a bubble.

In the case considered here the quantity h must be set equal to the thickness of the melt film. Since the latter is small, the hydrostatic pressure hgp in Eq. (5) can be neglected. We find the volume of a bubble by subtracting from the volume of a sphere of radius r_0 the volume of a spherical segment:

$$V = 1/3\pi^3(2 - 3\cos \theta + \cos^3 \theta). \quad (6)$$

The contact radius of a bubble equals [6]

$$r_{cr} = r_0^2 (2\rho g/3\sigma_{liq})^{1/2}. \quad (7)$$

After substituting into Eq. (5) the expression for the volume V (6) we obtain

$$r_0 = \frac{2\sigma_{liq} \sin \theta (2\rho g/3\sigma_{liq})^{1/2}}{1/3\pi g(6 + 3\cos \theta - \cos^3 \theta)}. \quad (8)$$

The wetting angle measured at 1273 K for $0.33\text{Na}_2\text{O} \cdot 0.67\text{SiO}_2$ melt is 15° ; $\sigma_{liq} = 0.286$ N/m [5]. Hence $r_0 = 0.52$ mm.

Taking the bubble as $h \approx 2r_0 \approx 1$ mm we arrive at the conclusion that a melt film with thickness $\delta < 0.2$ mm formed during pressure working of metals is appreciably less than the critical size of a bubble, and for this reason it can be expected that the bubbles released will break through the melt film, partially denuding the surface of the metal. For

this reason, together with the previously examined reactions in which hydrogen H_2 is released [1, 2] iron is oxidized directed by atmospheric oxygen (3) and water vapor (4). Since both processes can be excluded, oxidizing iron in the volume of the melt, their role can be evaluated by comparing the oxidation rate of iron under a film of thickness 0.2 mm and in the volume of the melt. Hence it follows that the reactions (3) and (4) play a large role in the total oxidation process.

The experimental data show (Fig. 2) that the average oxidation rate of 08kp steel over 10 min in air and water vapor ($p_{\text{H}_2\text{O}} = 40$ kPa) at 1273 K is 270 mg/(cm² · h); when a 0.2 mm thick film consisting of glass melt containing 0.33Na₂O and 0.67SiO₂ is deposited, it is almost an order of magnitude less and is approximately 34 mg/(cm² · h).

During the firing of the enamel the surface of the metal is bared as a result of gas being released; craters are formed and intense oxidation of the metal occurs there with the enamel melt being enriched with iron oxides, which results in the formation of copper-head and bubble-streak defects. As one can see from the data obtained, to avoid the formation of through craters in the enamel melt and decrease the formation probability of these defects the enamel coating must be at least 0.2 mm thick.

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